Hydrothermal Synthesis of Manganese Disulfide and Its Electrochemical Behavior

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Thermal batteries are used as the primary power sources for the nuclear weapons that are designed by Sandia National Laboratories (SNL) for the Department of Energy (DOE) [1]. In order to evaluate alternative cathode-active materials, we have begun a cooperative research program with Eagle-Picher Technologies, LLC to synthesize and evaluate the electrochemical characteristics of various first-row transition-metal disulfides. In this presentation, we present preliminary data for the preparation of manganese disulfide using hydrothermal conditions (~140°C and 365 kPa). Furthermore, we will present the discharge characteristics of this material in single cell tests at 250, 275, and 300°C.

When a 0.53 M aqueous solution of manganese sulfate was added to a 0.76 M solution of sodium tetrasulfide, a copious precipitate of manganese sulfide was formed. The pH of the mixture was brought to ~12 using 5 N NaOH. The resulting mixture was transferred to an autoclave and heated at ~140°C for 20 hrs. At this temperature, the reactor developed a pressure of nearly 365 kPa (53 psig). Extraction of the red-brown solid with CS_2 followed by solvent washing yielded nearly quantitative amounts of manganese disulfide. X-ray diffraction (XRD) analysis identified the synthesized material as Hauerite (MnS_2) with a pyrite (cubic) structure. The crystallite size, as calculated from full-width at half-maximum of the diffraction peaks, was ~120 nm. Elemental analysis of the synthesized material also confirmed the MnS_2 composition with a S/Mn ratio of 1.91

The XRD particle size results were somewhat inconsistent with scanning electron microscopy (SEM) investigations that revealed ~100 nm cubic crystals on micron-size cubo-octahedral crystals shown in Figure 1.

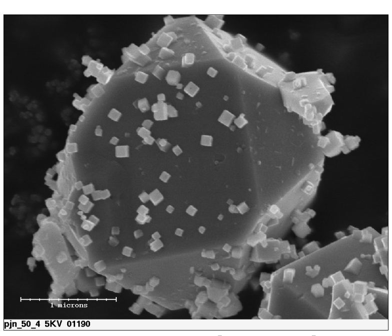

Figure 1. SEM image showing the crystal morphology of synthesized and purified MnS_2. Marker is 1 micron.

Thermogravimetric analysis (TGA) of MnS_2 in an argon atmosphere and heating rates of 10°C/min showed that thermal decomposition starts at ~410°C and is complete by 450°C. The ~26% experimentally observed weight loss is consistent with a theoretical expected weight loss of 26.9% for the formation of sulfur and MnS. Based on first order kinetics for the decomposition of MnS_2, an activation energy of 352 kJ/mole was found. The temperature range over which the decomposition takes place suggested that manganese disulfide might be useful as a cathode-active material for thermal batteries at the lower end of their operating temperature, i.e., 300 to 400°C. This temperature range is ideal for thermal batteries used in geothermal applications such as borehole data logging devices since it is above that for ambient-temperature lithium batteries and below that that for standard thermal batteries.

Anode pellets were pressed from a mixture of 75% Li(Si)-alloy blended with 25% alkali-metal bromide low melting eutectic[2] (LiBr-KBr-CsBr). The separator pellet was 35% MgO made with the same electrolyte. The cathode pellet was pressed from 80% MnS_2, 18.5% low melting eutectic, and 1.5% lithium oxide on a Grafoil™ disc. Single cells consisting of a stack of anode, separator, and cathode pellets sandwiched between stainless steel current collector and mica cover plates were assembled in a dry room. The 3.18 cm diameter cells were discharged between heated platens in a glovebox filled with high-purity argon. A steady-state load of 0.060 A (8 mA/cm^2) was used with a 0.125 A (16 mA/ cm^2), 1000 ms pulse applied every 60 s. The cells were tested at temperatures of 250, 275, and 300°C.

The test results for discharge of a Li(Si)/LiBr-KBr-CsBr/ MnS_2 cell at 300°C are presented in Figure 2. As shown, the cell exhibits ~2 V for most of the discharge reaction.

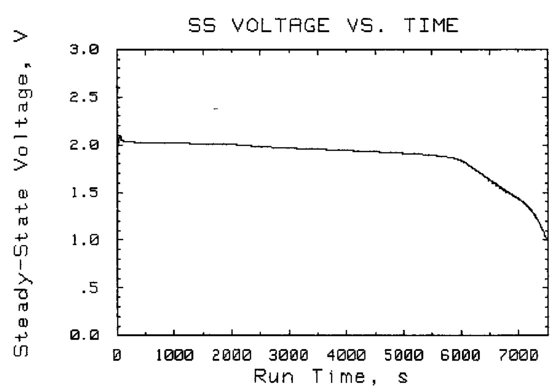

Figure 2. Steady-State Voltage vs. Time at 300°C for a Li(Si)/LiBr-KBr-CsBr/ MnS_2 cell.

The implication of the test results will be discussed in greater detail at this meeting.

Acknowledgements
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References

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